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POLYACETYLENES OF *ARTEMISIA VULGARIS*

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Abstract—During a re-examination of *Artemisia vulgaris*, a series of new acetylenic products, in addition to those previously known, was found. Trideca-1,3,5-triene-7,9,11-triyne and tetradeca-4,6-diene-8,10,12-triyne-1-ol, new compounds to the species, were fully characterized from the root extract, and heptadeca-1,7,9-triene-11,13,15-triyne, *cis*-dehydromatricaria ester and tetradeca-6-ene-8,10,12-triyne-3-one were found in the flowers, previously stated to contain no polyacetylenes. Three further polyacetylenes, known from related plants of the Anthemideae, were not fully characterized, but their presence was indicated.

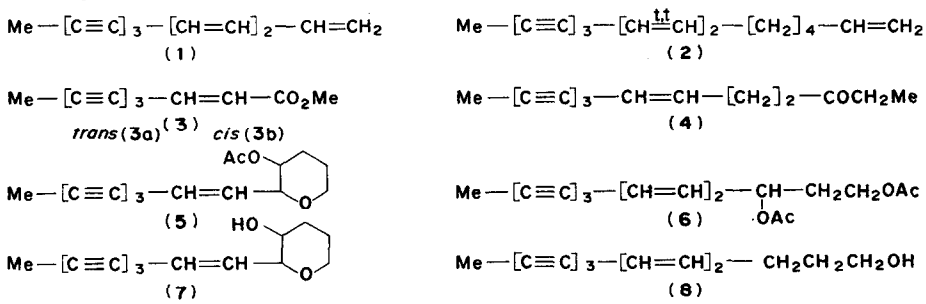
INTRODUCTION

THE COMMON Mugwort (*Artemisia vulgaris* L.) has been examined earlier for its polyacetylene content.[1–4] In view of the progress in instrumental and extractive techniques since these investigations, it was decided to re-examine the whole plant, especially the flowers, previously stated to contain no acetylenes.[1]

It has also been reported[4] that only *trans*-dehydromatricaria ester (**3a**) could be detected in plants harvested in late October, whereas only the *cis*-isomer could be detected in plants collected in June. Thus, the plant was harvested twice during the course of the present investigation and the content of **3a** and **3b** measured in each case.

RESULTS AND DISCUSSION

The crude plant extracts were chromatographed on silica gel columns, fractions containing the same compounds (as assayed by UV spectroscopy and qualitative TLC) were combined and purified by preparative TLC on silica gel.



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Roots

Two compounds were eluted together from the column by 2% Et_2O in light petroleum. Separation of the mixture by TLC revealed the two compounds to be a triyne-triene (λ_{max} 357, 334, 314, 285 and 273 nm) and a triyne-diene (λ_{max} 348, 326, 308, 290, 271 and 261 nm). The first compound was identified as trideca-1,3,5-triene-7,9,11-triyne (**1**)[5] by co-chromatography with an authentic sample. The second compound occurs in much larger amounts in the flowers and the two fractions were combined and purified. The IR spectrum showed the presence of acetylenic bonds (2220, 2180 cm^{-1}) and ethylenic bonds (1640 cm^{-1}) which could be further identified as a vinyl group (985, 908 cm^{-1}) and a CH≙CH–CH≙CH grouping (980 cm^{-1}). The MS showed a molecular ion at *m/e* 222, corresponding to a molecular formula of $C_{17}H_{18}$. The compound was identified on the basis of these data and co-chromatography with an authentic sample as heptadeca-1,7,9-triene-11,13,15-tyrine[2] (**2**).

A compound with a triyne-dienone chromophore (λ_{max} 343, 321, 301, 283, 257 and 246 nm) was eluted from the column by 10% Et_2O in light petroleum. The IR spectrum showed the presence of C≡C (2220, 2190 cm^{-1}), an α,β-unsaturated ester (1720 cm^{-1}) and a CH≙CH group (1620, 955 cm^{-1}). This compound was identified as *trans*-dehydromatricaria ester[6] (**3a**) by co-chromatography. The *cis*-isomer[1,6] (**3b** was eluted from the column by 15% Et_2O in light petroleum (λ_{max} 346, 323, 304, 287, 256 and 246 nm). IR: –C≡C– (2220, 2190 cm^{-1}), CH=CH–CH_2Me (1720 cm^{-1}), CH≙CH (1600, 690 cm^{-1}). NMR: $C\underline{H}_3$–C≡C– (3H, *s*) 7·95 τ, $CO_2C\underline{H}_3$ (3H, *s*) 6·25 τ, C<u>H</u>≙CH (1H, *d*, *J* 11·5 Hz) 3·28 τ, CH≙C<u>H</u> (1H, *d*, *J* 11·5 Hz) 3·83 τ.

A compound with a triyne-ene chromophore was eluted from the column by 20% Et_2O in light petroleum (λ_{max} 329, 308, 289, 273, 258 and 244 nm). IR: C≡C (2220, 2195 cm^{-1}), C=O (1735 cm^{-1}), CH≙CH (1600, 945 cm^{-1}). NMR: $C\underline{H}_3$–CH_2 (3H, *t*, *J* 7 Hz) 8·9 τ, $C\underline{H}_3$–C≡C (3H, *s*) 8·0 τ, R–CO–$C\underline{H}_2$–Me (2H, *q*, *J* 7 Hz) 7·65 τ, C≡C–$(C\underline{H}_2)_2$–CO (4H, *m*) 7·55 τ, <u>H</u>C≙CH–CH_2 (1H, *d*, *J* 16 Hz) 4·5 τ, HC=C<u>H</u>–CH_2 (1H, *m*) 3·7 τ. The MS showed a molecular ion at *m/e* 198, corresponding to a molecular formula of $C_{14}H_{14}O$. These data lead to the compound having structure (**4**).[1,2]

Small amounts of a compound with a triyne-ene chromophore were eluted from the column by 25% Et_2O in light petroleum (λ_{max} 329, 308, 290, 271, 259 and 244 nm). This compound was identical in its chromatographic behaviour to (**5**),[7] but insufficient material was present to allow complete characterization.

Two other compounds were eluted together by 50% Et_2O in light petroleum. One was a triyne-diene, the other a triyne-ene (λ_{max} 348, 325, 307, 289, 270 and 258 nm and 329, 308, 289, 273 and 243 nm, respectively). Again, insufficient material was available for full characterization, but chromatographic behaviour indicated the first compound to be (**6**)[8] and the second to be (**7**).[6–8]

75% Et_2O in light petroleum eluted a compound with a triyne-diene chromophore (λ_{max} 348, 327, 307, 290, 271 and 261 nm). The MS showed a molecular ion at *m/e* 198, corresponding to a molecular formula of $C_{14}H_{14}O$. The identity of the compound was estab-

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lished as tetradeca-4,6-diene-8,10,12-triyne-1-ol (**8**)[10] by chromatography with an authentic sample.

Compounds **1, 5, 6** and **8** are found in other species of *Artemisia*,[5,10–12] and **7** is known from other members of the Anthemideae.[13] The result of the investigation of **3a** + **3b** content is shown in Table 1.

TABLE 1. CONTENTS OF *cis*- AND *trans*-DEHYDROMATRICARIA ESTER IN PLANTS OF *Artemisia vulgaris* COLLECTED IN JULY AND SEPTEMBER

	Crop I (late July)		Crop II (early Sept.)	
	(mg/kg)	(%) of total	(mg/kg)	(%) of total
3a	1·42	14	0·4	3
3b	8·45	86	13·3	97

Thus, it would appear that the amount of *cis*-isomer increases during the growing course, and does not, as expected from earlier work,[4] decrease. However, the different treatment of the roots in the present investigation as compared to that in the previous work[1,4,6] (involving steam distillation) which is remarkably harsh treatment to give labile compounds, must be considered when comparing the results.

Flowers

Chromatography of the flower extract yielded relatively large amounts of **2**, and trace amounts of **3b** and **4**. A further compound with a slightly lengthened triyne-ene chromophore (λ_{max} 334, 312, 293, 277, 262 and 240 nm) was eluted from the column by 15% Et_2O in light petroleum. Insufficient material was again available for full characterization.

EXPERIMENTAL

A. vulgaris plants were collected near Terp north of Aarhus on dry soil during late July 1972. Further plants were collected from the same place 6 weeks later (a voucher specimen is preserved in our laboratory). The plants were washed, separated into roots, aerial parts and flowers, minced and extracted for 24 hr at room temp. (Roots were extracted with Et_2O, the flowers and aerial parts with petrol.) The solvent was removed from the extracts by filtration and concentrated by evaporation and weighed. Only the extracts from the roots and the flowers showed polyacetylenic content when assayed by UV. 1·0 kg roots yielded 1·85 g crude extract and 1·56 kg flowers yielded 9·56 g crude extract. The extracts were chromatographed on silica gel (Merck) columns made up in petrol. Preparative TLC was performed on 2·5 mm thick layers of silica gel G (Merck), using petrol. containing various proportions of Et_2O as eluting solvent. NMR spectra were recorded in $CDCl_3$ soln.

The following amounts of the compounds were isolated: *Roots*: mg/kg 0·05 **1**; 1·55 **2**; 1·4 **3a**; 8·5 **3b**; 17·4 **4**; trace **5**; 0·2 **6**; trace **7**; 1·2 **8**. *Flowers*: mg/kg 10·9 **2** and traces of **3b** and **4**.

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